Transport of Gas and Solutes in Permeable Estuarine Sediments

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LONG-TERM GOALS

The long-term goals of this project are to 1) quantify gas bubbles and their composition in shallow nearshore marine sand and 2) to assess the role of gas bubbles in shallow sandy coastal sediment for the transport of solutes through the sand and sediment-water exchange of matter. Due to their compressibility, gas bubbles embedded in shallow water sediments cause interstitial water oscillations under passing surface gravity waves, and these oscillations provide a mechanism for enhanced solute dispersion and flux.

OBJECTIVES

1) To detect gas bubbles and in coastal and estuarine sand deposits and to assess temporal and spatial distribution of sedimentary bubbles in sublittoral beds including sands inhabited by microphytobenthos and seagrass.
2) To quantify the size range and composition of the gas bubbles in the sediment and the overlying water.
3) To determine the volume change and migration velocities of interstitial bubbles and the links to pressure oscillations
4) To assess dispersion and transport of solutes caused by bubble volume change and migration under different pressure conditions.

APPROACH

For a more detailed description of the methods and technologies listed below we refer to the first annual report.

- *Measurement of gas release volumes from the sediments using benthic chambers and gas analysis.* Release rates and volumes of gas released from the sandy sediments are measured using benthic advection chambers.

- *Determination of gas composition.* The composition of the sampled gas volumes is analyzed using a Gas Chromatograph (GC).

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14. ABSTRACT
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15. SUBJECT TERMS

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- *Measurement of gas bubble dimensions and distribution.* Bubble size analyses are performed using ultrasonic and optical methods on sediment cores maintained at in-situ pressure, light and temperature and without changing the orientation of the core.

- *Mapping of the spatial and temporal distribution of high sedimentary photosynthetic production and oxygen supersaturation and depletion as potential sites for free gas development.* Measurements with an in-situ fluorescence detector and an oxygen microprofiler are used to map areas of benthic photosynthetic oxygen production.

- *Determination of the rate of gas bubble release from the sediment through quantification of noble gas depletion in the pore water.* With the GC, we measure the composition of the sedimentary gases including the noble gases. Pore water profiles of noble gases then can be compared with the volume of free gas detected in the sediment.

- *Determination of gas content, distribution and migration in the surface sediment.* Content, distribution and migration of free gas in the surface layers of the sand sediment is investigated with a tunable ultrasound square wave pulser, with measurement rate adjustable from 10 Hz to 1000 Hz in 10 Hz increments connected to one sending and one receiving high-frequency transducer (1-30 MHz).

- *Measurement of solute transport caused by bubble compression and migration.* This process is investigated in a laboratory column setup which allows measurement of the migration behavior and velocities of gas bubbles in permeable sandy sediments under the influence of sinusoidal pressure oscillations and determination of transport rates, dispersion and interfacial flux of solutes and colloidal material.

Participating Scientists and students. Scientists and students participating in this work are Dr. Markus Huettel (PI) responsible for all research in this project, field and lab experiments, technology development, data evaluation and publication work, Dr. Richard Wildman (Postdoc), responsible for ultrasound technique development, field measurements and pressure column measurements, Chiu Cheng (graduate student) responsible for flux measurements and field measurements, Fara Ilami (graduate student) responsible for flux analyses, Veronica Cruz (undergraduate student) support with field and laboratory measurements and analyses.

WORK COMPLETED

Field sampling and natural bubble creation. Exploratory field measurements of bubbles were made at two potential sandy field sites, the beach near the Florida State University Coastal and Marine Laboratory (CML) and St. Joe Bay (SJB). At CML, 20-30 cores were collected that covered all phases of the tide and times of day. At SJB, triplicate cores were collected during slack high tide shortly after noon. These sediment cores with visible gas bubbles were analyzed for free gas content. Cores were 10 cm long with a diameter of 3.5 cm. Gas extraction revealed that the sediment did not contain bubbles beneath a depth of ~3 cm. The gas bubbles originate from photosynthetic production of the dense diatom algae community growing in the upper sediment layer. Larger volumes (120 dm^3) of sand with bubbles were collected, brought to the laboratory, and illuminated with sunlight or fluorescent light to investigate bubble production in surface sands under controlled conditions.

Effect of ebullition on subsurface-surface solute exchange. The effect of ebullition, the movement of bubbles from one medium to another, on inert solute tracer transport through coarse-grained sediment (particle size 150-250 μm) was quantified using 5.5 cm and 19.0 cm diameter sand cores. Sediment pore water was stained with Fluorescein or Rhodamine WT dye to a final concentration of 100 μM. Small air bubbles were released through a nozzle positioned at incremental depths beneath the sediment surface. A series of experiments was run with gas release at 2.5, 2.0, 1.5, 1.0, 0.5 and 0.3 cm below the sand surface. Clear, deionized water was added above the sediment surface, and gas release rate was adjusted to 13.5 mL min^{-1} corresponding to approximately 60 bubbles per minute at 0.3 cm release depth. Control cores were set up identically with no gas flow through the sediment and diffusion as the only transport mechanism for tracer dye. A Turner Cyclops 7 fluorescence sensor read the concentration of dye in the water column over time. Diffusion and ebullition trials were run in parallel.

Development of ultrasonic detection methods. The Epoch XT, a hand-held ultrasonic instrument, emits and receives sound at one or two transducers with cross sectional area 1.25 cm^2. The instrument operates at frequencies of 0.1 to 1 MHz, allowing excitation of resonance frequencies for bubbles of the size we expect in surface sediment (Anderson and Hampton 1980). With the higher frequency we achieve size resolution in the sub-millimeter range in the upper tens of centimeters of the sand bed suited for the detection of small oxygen and methane bubbles abundant in the surface layer of coastal sands. The measurements with artificially-created air bubbles in both seawater and sediment were designed to assess 1) the speeds of sound in sand and sea water from our study site, 2) the sound reflection of a defined number of small gas bubbles 3) the modification of the waveforms caused by very small bubbles, allowing detection of the onset of bubble evolution in the sediment. 4) characteristics of waveforms collected from sand containing natural bubbles produced by photosynthesis and control sediment without bubbles.

Set up of the pressure tank experiments. The set-up of the experiments to evaluate both the effect of pressure on sediment-bound bubbles and the movement of these bubbles through the water column is partially complete. The acrylic rectangular base column 10 × 10 × 50 cm in size, is mounted vertically on a bottom piece containing an opening that allows insertion of a nozzle for addition of bubbles to the sediment from below. Bubbles in the water column are measured with particle image velocimetry and shadow imaging; the laser, strobe light, and CCD camera for these measurements have been positioned around the tank. An additional rectangular column permits doubling the height of the tank. This piece is equipped with an angled top that directs bubbles towards a sampling port on the side of the tank. The water-tight tank is pressurized by a computer-controlled linear pump allowing simulation of wave and tide patterns. A 400 W metal vapor lamp has been purchased to provide light of color temperature 6500 K, which has a wavelength resembling that of the sun. Positioning this above the tank will permit bubble growth in the incubated sediment by photosynthesis.

RESULTS

Fieldwork and bubble production. At CML, ample bubbles were observed during a scouting trip, but none were present when quantitative measurments were attempted. We attribute these observations to weeks of calm conditions that preceded the scouting trip and several days of storms (which would have induced resuspension of sediment and disruption of photosynthetic benthos) in the two weeks preceding the second trips. At SJB, triplicate samples collected from sandy sediments with gas bubbles produced by photosynthesis indicated that gas concentrations reached 5% of the upper 5 mm sediment layer. In laboratory experiments with freshly retrieved sediment oxygen bubbles evolved one hour after sediment exposure to sunshine producing an ebullition rate of ~36,000 bubbles m^{-2} h^{-1} when exposed to bottom current of typical magnitude (10-30 cm s^{-1}). Embedded bubbles formed within the upper 3 mm of the sediment. The largest bubbles created reached ~0.845 mm in diameter. Without bottom current or sunlight to continue gas production, bubbles remained in place (i.e., embedded in a given location in the sand) overnight. This suggests that gas in sediment is not necessarily a product of that day's photosynthetic activity.

Ebullition. Bubble ebullition caused a significant increase of inert dye flux from sediment into the overlying water compared to diffusive transport (Figure 1). For the same gas volume flow, the shallower the sediment depth of bubble release, the larger the flux of the dye. The shallower bubble release depth resulted in higher bubble ebullition frequency compared to the deeper bubble release producing fewer large bubbles and ebullition at lower frequency. This suggests that the rate of bubbling, not the volume of gas flow, is the dominant parameter for solute flux. Future work will replace fluorescein with an environmentally-relevant solute, such as phosphate, and additional trials will evaluate bubbling rate, production of multiple bubbles, and sediment area affected by each individual bubble.

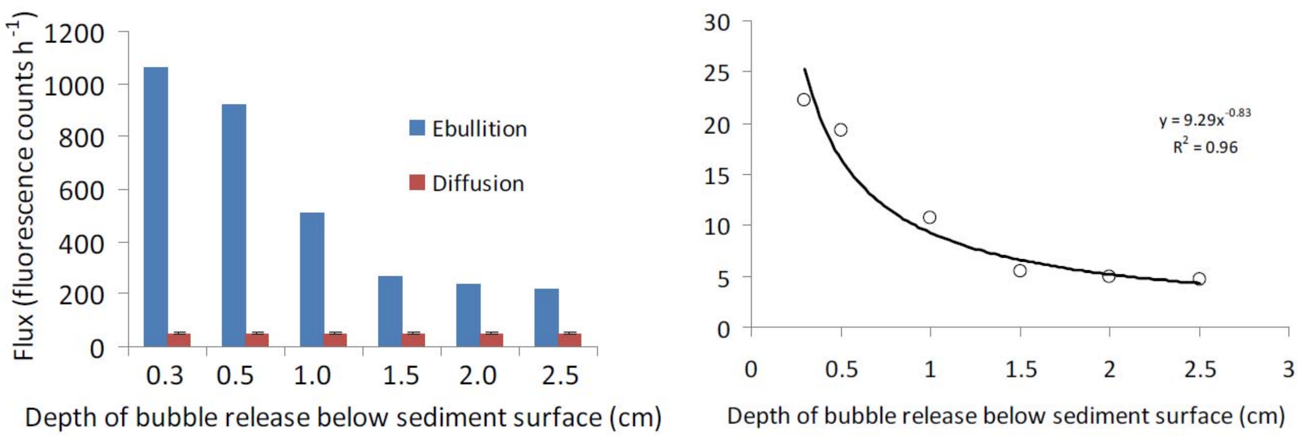

Figure 1, ebullition experiments. Left panel: Bubble-enhanced flux (in relative fluorescence units, RFUB) versus diffusive flux for varying depths of gas release beneath the sediment water interface. Rright panel: The ratio of bubble-enhanced flux versus diffusive flux for varying depths of gas release demonstrating the strong effect of the bubbles on solute flux.

Bubble detection. Measurements of the speed of sound in water and sand produced sound velocities of 1507 and 1797 m s^{-1}, respectively (Figure 2, left). These are in line with published values of 1500 ± 20 m s^{-1} and 1760-1800 m s^{-1} for sound velocities in water and sand, respectively (Wille 2005, Thorsos 2001). The strength of the ultrasonic signal emitted from one transducer and received by a second transducer is attenuated by small bubbles added one by one into the path of the ultrasonic beam (Figure 2, right). Bubbles in the size range of 0.3 µL can be detected with this method. Attenuation increases with bubble size. With the transducers used, 3 small bubbles (1 µL in size) produced a detectable decrease in the sound pulses.

Our ultrasound technique permits analyzing the reflected ultrasonic signal for the effect of bubbles embedded in sand. Bubbles produced in the sand (here by electrolysis at a buried wire), change the amplitude of the ultrasound pulse (Figure 3, left). The peaks that occur earlier (i.e., at a smaller time of flight) indicate that bubbles moved above the location of bubble generation. In submerged sediment containing bubbles created by sunlight, we observed differences in waveforms collected in sand with and without bubbles (Figure 3, right pane). The missing peak in the reflection signal collected in sand without bubbles demonstrates that small bubbles in the µL range can be identified nondestructively beneath the sand-water interface using this low energy ultrasound technique.

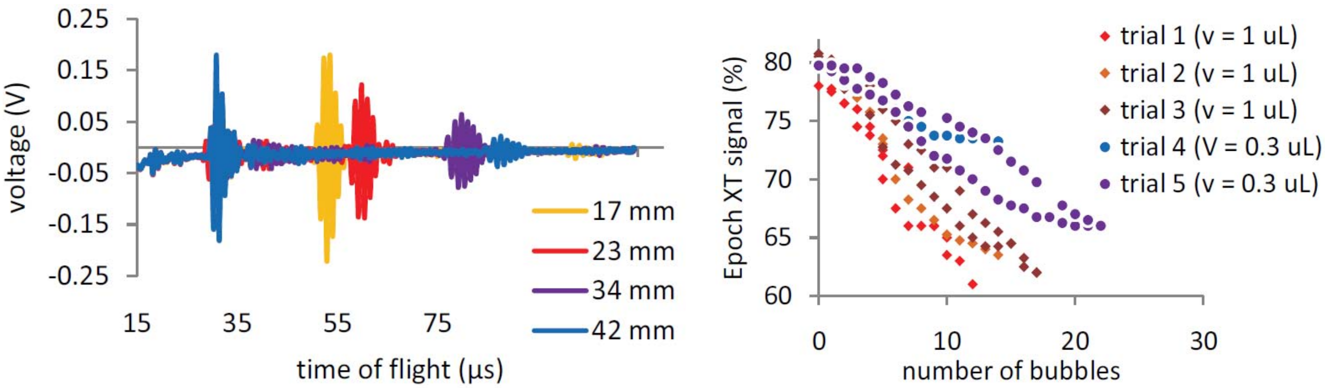

Figure 2, left pane: waveforms of ultrasonic waves penetrating sand of different depths and reflecting back to the emitting transducer, which was 23 mm above the sediment-water interface. Overlapping peaks at about 30 µs represent the sediment water interface. Later peaks at 50 µs and greater are the reflection off the bottom of the sand layer. The Epoch XT was operated at 200 V and 1 MHz. At these settings, it appears that the sound signal will be fully attenuated 50 mm into the sand. Right pane: degradation of ultrasonic signal by incremental addition of bubbles.

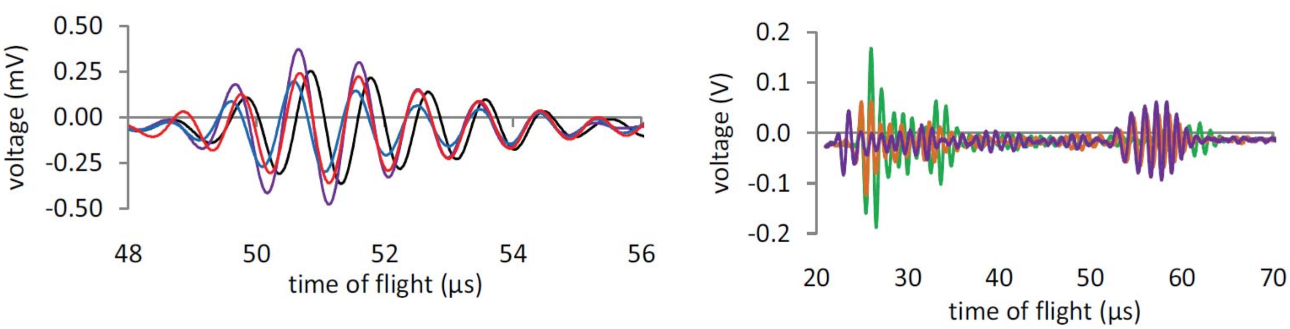

Figure 3, Left pane: Effect of bubbles on ultrasound waveform shape. Black wave: signal without bubbles. Purple, blue, and red waves: signal with 0.070 mL, 0.139 mL, and 0.278 mL of gas in the sediment, respectively. Inconsistent effects are due to ebullition, since the volume estimates result from the volume of gas produced on the wire, and ebullition releases some of this out of the sand. Right pane: Effect of bubbles on ultrasonic reflection. Green: sediment containing bubble. Purple and orange: signal after bubble release. Peaks in the green waveform at 30-35 µs are caused by bubbles. Peaks at 20-30 µs represent sediment-water interface. Peaks at 50-65 µs are the reflection of the bottom of the sediment container.

IMPACT/APPLICATIONS

Our field observations in the northern Gulf of Mexico indicate that the amount of bubbles produced by benthic photosynthesis is substantial and reaches 5% of sediment volume in the upper 3 cm of shallow sand sediments. This high production of bubbles facilitates sediment water exchange that significantly increases fluxes of solutes. The initial oxygen bubbles equilibrate with other gases dissolved in the pore water according to the prevailing partial pressures and thus become a vehicle for sulfide, methane and carbon dioxide from sediments to the atmosphere. We developed an ultrasound technique that for the first time permits non-invasive detection of small bubbles in the surface layers of marine sands. This technique can be used to quantify bubble size, number of bubbles and burial depth of bubbles in sandy beds.

The release of small bubbles significantly enhances solute flux from the sediment, increasing inert tracer fluxes relative to diffusion 5 to 22-times. As the release of fluid from the sediment caused by the bubbles is balanced by the same amount of fluid penetrating into the sediment, bubble release causes water intrusion into the bed that reaches as deep as the bubble release depth. The bubble-related transport thus can release nutrients and carbon dioxide from the sediment and transport oxygen into the sand. Our experiments indicate that one 80 µL bubble released from 1 cm sediment depth causes the release of approximately 3 µL pore water. With natural release of bubbles measured at our study site (36000 m^{-2} h^{-1}), this translates into fluid fluxes of 1.14 L m^{-2} d^{-1} from the sediment (for a day with 10h photosynthetic gas production).

Laboratory tests showed that oxygen-containing gas bubbles can persist in the sediment over longer time periods (at least 24h) even under dark conditions if no ebullition occurs. Cumulative effect thus can be expected in shallow sediments where bubbles can build up during calm periods over days before they are released by increasing bottom currents. The consequences of this effect include pulses of nutrients and contaminants released from the sand beds and pulsing gas emission to the atmosphere.

With the technologies developed in this project we now are able to quantify the bubble accumulation in the surface layer of sandy coastal sediments and investigate the effects of pressure oscillations as caused by waves and tides on the gas and solute release associated with embedded gas bubbles. Future research will address the transport of particulate matter by the gas bubbles and the effect of the emerging bubbles on mixing and solute distribution in the water column.

The relevance of these processes is associated with the increasing coastal eutrophication caused by anthropogenic nutrient release to the continental shelves. The ensuing enhanced primary production increases oxygen bubble generation while the enhanced organic matter sedimentation increases methane, carbon dioxide and sulfide production in coastal sediments. We therefore expect that the impact of gas bubbles on ecosystem functions will increase and the hypoxic zones developing in the Northern Gulf of Mexico and many other coastal areas show dramatically the increase of sedimentary gas production when organic matter processing is completed entirely by microbial processes. Gas bubble research thus will gain momentum and our research and developments support these future investigations.

TRANSITIONS

At this stage of the project, there are no outside users of the project results.

RELATED PROJECTS

Collaborative research: Degradation of dissolved organic matter in permeable sediment, NSF-OCE-0726754, 9/1/07-8/31/10, $599,636, Markus H. Huettel (PI), Joel E. Kostka (co-PI), Thorsten Dittmar (co-PI), William T. Cooper (co-PI) The objectives of this ongoing research are 1) quantification of DOM degradation in filtering Gulf of Mexico sands and overlying water 2) assessment of the influences of pore flow velocity, temperature, oxygen concentration and light on DOM decomposition rates, 3) characterization of DOM compositional changes caused by sediment passage and 4) quantification of the abundance of metabolically active prokaryotes and establishment of a direct linkage between DOM metabolism and the phylogenetic composition of microbial communities, 5) integration of the results into an empirical model that quantitatively relates DOM degradation rates to pore water velocity, temperature, oxygen and light. Our methodological approach combines column reactor experiments with state of the art DOM analyses and molecular microbial community investigations including Stable Isotope Probing. Advection chambers are deployed in-situ to validate model predictions. ^{13}C-labeled labile and refractory DOM will be used as a traceable and quantifiable substrate. Sedimentary DOC degradation causes oxygen consumption and enhances primary production through nutrient remobilization.

NSF project "Further Development of the Eddy Correlation Technique; NSF-OCE-0536431; 01/01/06-12/31/10; $742,717; P. Berg, (PI), M. Huettel (co-PI). This ongoing project was awarded as a follow-up of our first eddy correlation project (OCE-0221159) and supported continuation of our research and instrument development related to the eddy correlation technique for the measurement of oxygen flux in permeable coastal sediment. In addition to intensive field campaigns at the two main field sites, the Virginia Coast Reserve LTER site and the Apalachicola NERR site, we have visited several other sites that appeared particularly challenging with respect to flux measurements. These include the rocky bottoms in The Great Lakes with dense colonies of the invasive Quagga mussel overgrown with filamentous algae (Fig 1A – in collaboration with the Great Lakes WATER Institute, WI) and the deep ocean floor off the coast of Japan (Fig 1B – in collaboration with JAMSTEC, Japan). Data from these sites have provided both new insights on benthic oxygen metabolism and a demonstration of the advantages of the eddy correlation technique in diverse environments.

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